Polymeric Fe(II) spin cross over compounds : XAS structural results

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Abstract. Fe(II)triazole derivatives are spin cross-over compounds with various T_C (-30->+150 °C), large thermal hysteresis ($\Delta T_C \approx 50$ K) and an important thermochromic effect. These promising properties, which are already used in experimental imaging and memory devices, are probably due to their polymeric structures. We have studied these structures by EXAFS and X-Ray diffraction (in spite of the important long distance disorder observed) . The key result of this study is the alignment of a long chain of Fe(II) ions in the Low Spin (LS) state of the polymeric species, proved by the presence of a characteristic double Fe-Fe distance multiple scattering EXAFS signal (analysed by FEFF code). New results have been obtained recently on new members of the Fe(II) triazole family and nickel glyoxime model compounds presenting similar metal-metal alignment, proving definitely the assumed alignment in the LS state. Systematic study of the temperature dependence of the multiple-scattering signal amplitude were performed in order to explain the apparent vanishing of the alignment in the High Spin (HS) state.

1. INTRODUCTION

Since they are badly crystallized, the polymeric Fe(II) triazole spin cross-over compounds structures can not be characterized properly by diffraction. In a previous paper [1], we have reported EXAFS results and proved that the structural model assumed to explain the large cooperativity (leading to a large thermal hysteresis) in their spin transition was almost correct. The purpose of this work is to give new experimental proves of our structural model for the LS state and try to explain why this model seems to fail in the HS state. The key result of our previous study was the discovery of an unexpected and uncommon EXAFS signal near 7 Å in the LS state of polymeric iron triazolates. It was proved that this peak was not due to an artifact but was necessarily the signature of a structural behavior. A distance of 7 Å is almost the double of the expected Fe-Fe distance in triazolate bridged dimers. Thus, it was logical to assume that this peak could be assigned to the multiple scattering Fe-Fe-Fe path (focusing effect). FEFF calculation with a model including such a long chain of aligned Fe(II) ions showed that our assumption was coherent. In order to prove it experimentally, we have decided to study the EXAFS spectra of two kinds of model compounds with known crystallographic structures : i) monomeric molecular systems similar to the polymeric systems in which there is no Fe-Fe-Fe alignment. In this case, EXAFS signal at 7 Å should be absent. ii) molecular inorganic compounds with well characterized metal-metal alignment in which the double multiple scattering distance should be observed. At least, the reason why the metal alignment is apparently not observed in the HS state of the polymeric triazolate Fe(II) compounds needed to be discussed in more details : powder diffraction results and the reversibility of the spin transition are apparently incompatible with a large structural change during the transition. We contribute to this discussion by studying the variation of the 7 Å multiple scattering signal amplitude with temperature between 80K (LS state) and 400K (HS state).

2. MATERIALS AND METHODS

[Fe(Htrz)2-(trz)(BF4) (polymeric triazolate compound) [2], Hexakis(1-propyltetrazole)iron(II) Bis(tetrafluoroborate) (monomeric tetrazolate analog to the polymeric triazolate), nickel(II)(dimethylglyoxime)$_2$ (molecular inorganic compounds with various metal alignments) were synthetized as described in the literature [3-4]. Their EXAFS spectra at the Fe K edge were recorded at 80K and 300K on the EXAFS 1 and EXAFS 3 ports (LURE DCI). In addition, the XAS spectra of the polymeric compound was also recorded at 355 K in both LS and HS states, since this temperature is exactly the middle point of the thermal hysteresis loop. The LS state at 355K was obtained by increasing T from the room temperature, while the HS state was reached by decreasing T from 420 K.
The samples were prepared as homogenous compressed pellets and their weight calculated in order to get an edge jump $\Delta\mu x \approx 1$. Standard EXAFS extraction and Fourier analysis were performed with "EXAFS pour le MAC" package [5]. All Fourier spectra are presented without phase correction. EXAFS modeling and fits used ROUND MIDNIGHT (from previous package) and FEFF [6].

These structures are presented on figure 1.

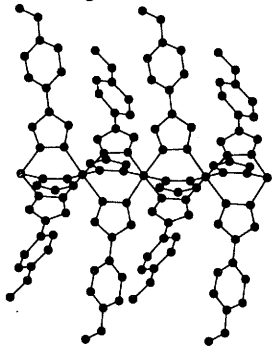

Figure 1-a: Assumed polymeric structure

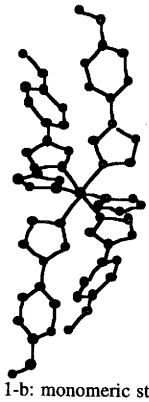

Figure 1-b: monomeric structure

3. RESULTS AND DISCUSSION

3.1 Structures of the monomeric Fe(II) tetrazolate [3] and the polymeric Fe(II) triazolate (assumed)

3.2 Comparison of monomeric tetrazolates and triazolates polymeric Fe(II) EXAFS spectra.

Figure 2 shows the Fourier transform (FT) modulus of the monomeric and the polymeric compounds in the Low Spin state at 80 K (Fig 2-a) and in the High Spin state (Fig 2-b). For the later case the temperatures are respectively 300K for the monomer and 403 K for the polymer since the LS->HS Tc for this compound is 390 K.

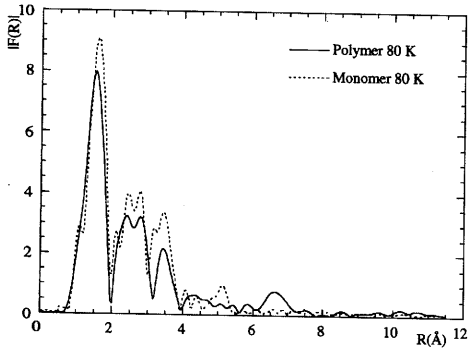

Figure 2-a: Fourier transform modulus in the LS state

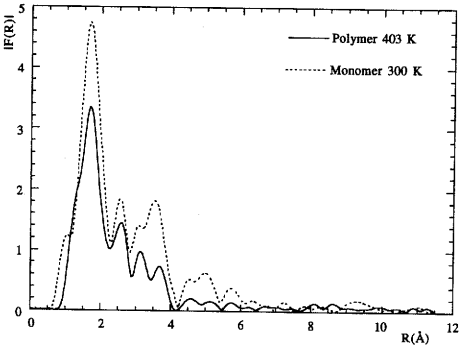

Figure 2-b: Fourier transform modulus in the HS state

As expected from the Fe(II) local order presented on figure 1, structures of monomer and polymer spectra between 0 and 4 Å are quite similar. Their differences should come from the presence of the bridged Fe-Fe distance at 3.5 - 3.7 Å for the polymer. In this range of distances, many single and multiple scattering paths involving the cyclic organic ligands are expected.

This assumption is confirmed by the presence of two strong EXAFS FT peaks between 2 and 4 Å in the spectrum of the monomer, where the absence of any Fe contribution is obvious. It was also confirmed by a FEFF simulation presented in ref. [1]. Thus, the Fe-Fe signal in the polymer is mixed and interfere with the low Z atoms contribution discussed above. This is the reason why the observed difference between the two spectra in this range of distances seems quite small. The presence of the iron atoms can be detected with more efficiency by the comparison of the FT imaginary parts (Fig. 3) : the two signals are out of phase near 3 Å. The most important difference between the two spectra in figure 2.a is the presence of a significant peak around 6.8 Å in the polymer spectrum (LS state). This peak is clearly absent for the monomer. **When there is no alignment of metallic centers, the peak at 7 Å is not observed.**

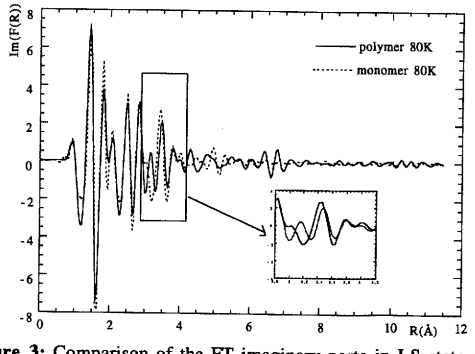

Figure 3: Comparison of the FT imaginary parts in LS state of polymeric and monomeric Fe(II) triazolate and tretrazolate

3.3 Metal alignment in a Ni(dimethylglioxine)$_2$ complex.

The possibility of detecting a M-M-M alignment by the presence of the multiple scattering focusing effect signal is shown in the study of the EXAFS spectra of Ni(dimethylglioxine)$_2$ at 80 and 300 K. The crystal structure of this compound is well known [3] : the planar complexes are stacked along the c axis with a Ni-Ni distance of 3.24 Å. The multiple scattering signal is clearly observed in the low temperature spectrum in figure 4. The difference between this case and the Fe(II) polymer is that here the Ni ions are not bridged by strongly bonding ligands. The Ni-Ni signals are not observed at room temperature since there are affected by strongly temperature dependent Debye-Waller factors. **When there is a known alignment of metallic centers, the multiple scattering peak can be observed.**

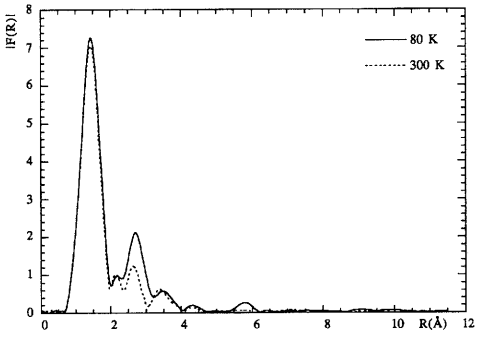

Figure 4: Modulus of the FT in Ni(dimethylglioxine)$_2$

3.4 Why the 7 Å peak of the polymer in the HS state is not observed ?

Figure 2.b is a confirmation of the absence of this peak in the spectrum of the Fe(II) polymer in the HS state.
This question has been already discussed in ref. [1]. Since the structure of the HS state cannot differ strongly compared to the LS state (the Fe-Fe bridges cannot be broken), we have retained two possibilities. i) The irons are not yet aligned and the enhancement of the 7 Å peak, due to the focusing effect, is lowered. ii) In the HS state, the 7 Å peak is affected by a strong Debye-Waller due either to a structural disorder or by an enhancement of the thermal vibrations, both induced by the Jahn-Teller effect at the Fe(II) site. Figure 5 represents the variation of the 7 Å LS peak between 80 and 355 K. The multiple scattering signal is only slightly temperature dependent, as expected for strongly bond aligned metals. **The disappearance of the 7 Å peak for the HS state can not be explained by a continuous temperature variation of the Debye-Waller factor.**

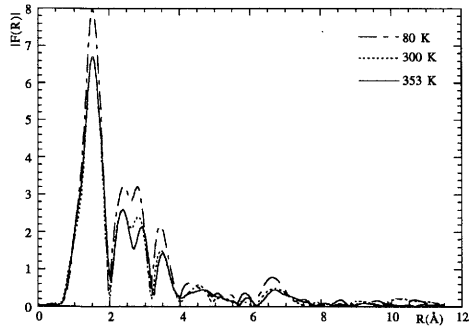

Figure 5: FT spectra of the polymeric compound in LS state

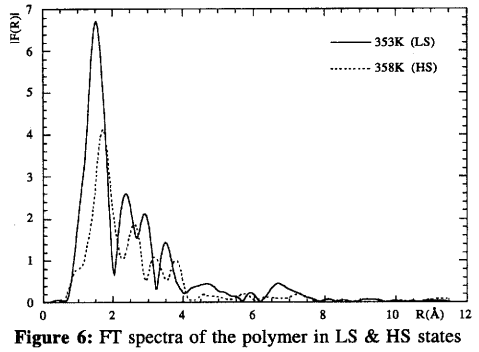

Figure 6: FT spectra of the polymer in LS & HS states

On figure 6, we present both LS and HS spectra at the same temperature (355 K). In the HS state, the 7 Å signal is strongly reduced. It seems to remain just above the noise level but cannot be considered as significant. Thus, it is impossible to assume from these EXAFS results that the alignment is destroyed in the HS state. But, our study proves that it is significantly perturbed. At higher temperature, the 7 Å signal is completely vanishing.

4. CONCLUSION

In this study, we have confirmed by two new experimental results the alignment of the Fe(II) ions in the LS state of [Fe(Htrz)2-(trz)(BF4) and the related the polymeric spin cross-over compounds. The reasons of the apparent disappearance of this alignment in the HS state were discussed in details. However, it is impossible from an EXAFS study to settle between a structural or a vibrational distortion. In order to try to answer to this question, we have recently performed complementary anomalous diffraction and scattering experiments. The data are under treatment.

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